

# Kongeriget Danmark

Patent application No.: PA 2002 01992  
Date of filing: 21 December 2002  
Applicant: Haldor Topsøe A/S  
(Name and address) Nymøllevej 55  
DK-2800 Kgs. Lyngby  
Denmark

Title: Fremgangsmåde til fjernelse af SO<sub>2</sub> af afgasser ved omsætning med H<sub>2</sub>O<sub>2</sub>

IPC: B 01 D 53/50

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



Patent- og Varemærkestyrelsen  
Økonomi- og Erhvervsministeriet

24 November 2003

Pia Høybye-Olsen

**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Modtaget

21 DEC. 2002

PVS



**HALDOR TOPSØE A/S**

NYMOLLEVEJ 55 · P.O. BOX 213 · DK-2800 LYNGBY · DENMARK · CVR NO. 41853816 · VAT NO. DK 41853816  
TELEPHONE: +45 4527 2000 · FAX: +45 4527 2999 · WWW.HALDORTOPSOE.COM

20 December 2002

DK389-7237003

HABS/AKN

**Process for Removal of SO<sub>2</sub> from  
Off-Gases by Reaction with H<sub>2</sub>O<sub>2</sub>**

The present invention relates to a process for removal of  $\text{SO}_2$  from off-gases by reaction with  $\text{H}_2\text{O}_2$ .

5 It has been known for more than 30 years that  $\text{SO}_2$ , as described in the publication 2164e from Lurgi/Südchemie AG, August 1989, can be removed from off-gases by contacting the off-gas in an absorption tower with circulating solution of dilute sulphuric acid containing  $\text{H}_2\text{O}_2$ , whereby  $\text{SO}_2$  is dissolved and oxidised to  $\text{H}_2\text{SO}_4$  in the solution. The  
10 circulating solution typically contains 30-60%  $\text{H}_2\text{SO}_4$  and 0.1-0.5%  $\text{H}_2\text{O}_2$ . The absorption is typically carried out at a temperature of 50-80°C of the circulating solution.  $\text{H}_2\text{O}_2$  is added either as a concentrated aqueous solution of  $\text{H}_2\text{O}_2$  to the circulating acid, or it is produced by electrolysis of  
15 a side stream of the circulating acid. The produced acid is drawn off from the circulating acid.

The known process usually requires installation of a low velocity aerosol filter downstream of the absorption tower  
20 to remove sulphuric acid aerosol (acid mist) in order to meet acid mist emission regulations requiring less than about 5 mol ppm  $\text{H}_2\text{SO}_4$  in the stack gas. Fine acid mist (aerosol) that may be present in the off-gas is not removed efficiently in the absorption tower. Fine acid mist is also  
25 formed in the absorption tower itself by reaction between  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  vaporised from the absorbing liquid.

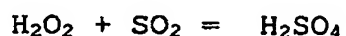
It is a disadvantage of the known process that it requires installation of both an absorption tower and a low velocity  
30 mist filter.

In the process according to the present invention,  $\text{SO}_2$  in off-gases is removed by reaction with  $\text{H}_2\text{O}_2$  without the use of an absorption tower by spraying a solution of  $\text{H}_2\text{O}_2$  in water or dilute sulphuric acid into the off-gas upstream of a low velocity aerosol filter or wet electrostatic precipitator (WESP).

A preferred embodiment of the invention is shown in Figure 1. A solution of 0.1-30%  $\text{H}_2\text{O}_2$  in line 1 is sprayed by the spray nozzles 3 into a stream of off-gas in line 2 containing typically between 100-1000 ppm  $\text{SO}_2$  and having a temperature typically in the range of 50-120°C. The nozzles are placed in duct 4, so that the spray is evenly distributed in the gas stream upstream of the mist filter 5 in which the gas is passed in parallel through a number of low velocity filter candles 6. Even distribution of the droplets in the gas is desirable for the process, and the most even distribution of the droplets is achieved by using air-atomising nozzles producing very small droplets. The  $\text{H}_2\text{SO}_4$  formed in the process accumulates in the filter elements or candles from which it is drained off through line 7. Most or all of the mass of the droplets evaporate before the gas enters the filter candles, whereby most of the  $\text{H}_2\text{O}_2$  evaporates and reacts in the gas phase under formation of sulphuric acid aerosol. However, it is not necessary that the droplets are completely evaporated before the gas enters the filter elements. The reaction between  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  will be completed and the thermal equilibrium will be established in the mist filter elements without decreasing the efficiency of the  $\text{SO}_2$ -removal.

Thus the injection of the aqueous solution  $\text{H}_2\text{O}_2$  serves two purposes:

5 Firstly, it adds to the off-gas the amount of  $\text{H}_2\text{O}_2$ , which is required for achieving the desired conversion of  $\text{SO}_2$  into  $\text{H}_2\text{SO}_4$  by the reaction



10 Most of the conversion takes place by reaction in the gas phase between  $\text{SO}_2$  and vaporised  $\text{H}_2\text{O}_2$  under formation of acid mist, or between  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  dissolved in the droplets. The reaction is completed in the aerosol filter in which re-  
15 tained in the dilute sulphuric acid wetting the fibre material.

Secondly, the water comprised in the solution cools off the off-gas in line 2 by evaporation of the droplets, whereby  
20 the off-gas is cooled off to a desired temperature of the filter elements or candles typically to a temperature between  $50^\circ\text{C}$  and  $70^\circ\text{C}$ . The concentration of  $\text{H}_2\text{SO}_4$  in the produced acid will be the equilibrium concentration of  $\text{H}_2\text{SO}_4$  at the actual temperature and  $\text{H}_2\text{O}$  partial pressure in the  
25 gas phase.

Up to 98%  $\text{SO}_2$ -removal can be achieved at, typically, about 95% utilisation of the  $\text{H}_2\text{O}_2$ .

**Example**

An off-gas stream of 1000 Nm<sup>3</sup>/h at 100°C contains 200 ppm SO<sub>2</sub> + 10% H<sub>2</sub>O and has a temperature of 100°C. 96% SO<sub>2</sub> removal is desired. The aerosol filter is designed for operation at maximum 70°C. Operation at 67-70°C is chosen in order to achieve the highest possible acid strength and low content of remaining H<sub>2</sub>O<sub>2</sub> in the produced acid.

The process is conducted as follows: 15.7 kg/h water containing 2.0 wt% H<sub>2</sub>O<sub>2</sub> is injected into the off-gas, whereby the off-gas is cooled to 65-70°C in thermal equilibrium. The mist filter is 75 mm thick and has a flow area of 2.5 m<sup>2</sup>. The diameter of the fibres is about 8 µm. Experiments carried out under these conditions show that about 96% of the SO<sub>2</sub> is removed under production of 1.7 kg/h 50% H<sub>2</sub>SO<sub>4</sub> with about 500 ppm H<sub>2</sub>O<sub>2</sub>. The treated gas contains less than 2 ppm H<sub>2</sub>SO<sub>4</sub>, and the content of H<sub>2</sub>O<sub>2</sub> is below the detection limit.

**CLAIMS**

1. A process for removal of  $\text{SO}_2$  in off-gases having a temperature of 30-150°C and containing 0.001-1 vol%  $\text{SO}_2$  in which the  $\text{SO}_2$  is oxidised to  $\text{H}_2\text{SO}_4$  by spraying an aqueous solution of  $\text{H}_2\text{O}_2$  into the off-gas upstream of an aerosol filter removing the produced sulphuric acid from the off-gas.  
5
- 10 2. A process as in claim 1 in which the off-gas is cooled by evaporation of the water comprised in the solution being sprayed into the off-gas upstream of the filter.
- 15 3. A process as in claim 1 in which a wet electrostatic separator is used in place of an aerosol filter.

**ABSTRACT**

5 A process for removal of  $\text{SO}_2$  in off-gases having a temperature of 30-150°C and containing 0.001-1 vol%  $\text{SO}_2$  in which the  $\text{SO}^2$  is oxidised to  $\text{H}_2\text{SO}_4$  by spraying an aqueous solution of  $\text{H}_2\text{O}_2$  into the off-gas upstream of an aerosol filter removing the produced sulphuric acid from the off-gas.



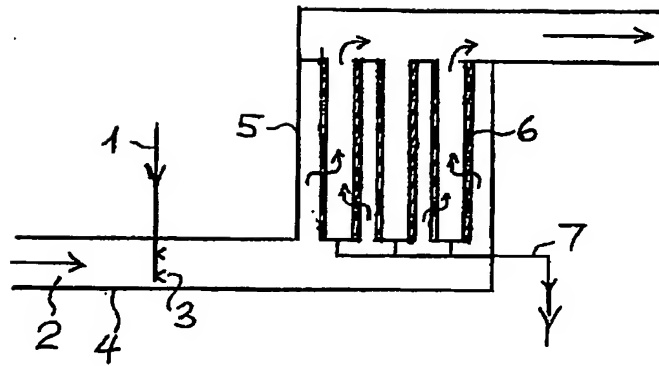


Fig1